Letters to the Editor

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ESTIMATION OF THE CRYSTALLINE ELECTRIC FIELD AND EVALUATION OF g-FACTORS IN $CuSO_4 . 5H_2O$

A. NARASIMHAMURTHY AND D. PREMASWARUP

MICROWAVE LABORATORY, ANDHRA UNIVERSITY, WALTAIR

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In $Cu(KSO_4)_2.6H_2O$ where the Cu^{++} ion is surrounded by six water molecules arranged with tetragonal symmetry, Polder (1942) calculated the induced and hence effective dipole moments of the two types of water molecules corresponding to the two different distances from the Cu^{++} ion. However, in the absence of any data on $Cu(KSO_4)_2.6H_2O$, Polder took the distance parameters the same as in $CuSO_4 . 5H_2O$ in which the nearest neighbours of the Cu^{++} ion are established as four equidistant water molecule and two equidistant oxygen atoms (of the SO_4 groups) distributed with tetragonal symmetry about the axis joining the two oxygen atoms according to the X-ray diffraction analysis of Lipson and Beevers (1934). These values are then utilised to calculate the strength of the crystalline electric field at the copper ion and the Stark energy splitting of the ground state. Results of this calculation were later used by Spence and Kikuchi (1950) to evaluate the principal g-values of the Cu^{++} ion in the $CuSO_4.5H_2O$ crystal. However, the effect of the very considerable differences in the values of the permanent dipole moments of water molecules and oxygen atoms (1.87D and 0 respectively) makes the calculation for this salt different from that of Polder. We have undertaken such calculations for $CuSO_4.5H_2O$ employing the method described in an earlier communication by us (1963) taking the oxygens as neutral atoms instead of $(SO_4)^{2-}$ groups in view of the large size of this group compared to the Cu—O distance.

Both the water molecules and oxygen atoms are regarded as point dipoles placed at the corresponding lattice points with distances $a = 2.0$Å and $b = 2.3$Å

respectively from the copper ion. Polarisabilities and permanent dipole moments of water and oxygen respectively are

$$\alpha H_2O = 1.48\times10^{-24}\text{cc} \qquad \alpha_O = 1.57\times10^{-24}\text{cc}$$
$$\alpha H_2O = 1.87\text{D} \qquad \mu_O = 0$$

Representing the effective dipole moments of the water molecule and oxygen atoms by μ_a and μ_b respectively, so oriented that their negative ends are towards Cu^{++}, one can write down from the fields at the different lattice points due to the surrounding charges and dipoles, the following equations.

$$\mu_a = \mu H_2O + \alpha H_2O\left[\frac{Ze}{a^2} - \frac{\mu_a}{4a^3} - \frac{3\mu_a}{2\sqrt{2}a^3} - \frac{6ab\mu_b}{(a^2+b^2)^{5/2}}\right]$$

$$\mu_b = \mu_0 + \alpha_0\left[\frac{Ze}{b^2} - \frac{12ab\mu_a}{(a^2+b^2)^{5/2}} - \frac{\mu_b}{4b^3}\right]$$

The field in the immediate neighbourhood of the paramagnetic ion can be represented as usual by

$$V_{cryst} = A_2^0 r^2 Y_2^0 + A_4^0 r^4 Y_4^0 - A_4^{\pm4} r^4 Y_4^{\pm4}$$

Numerical values of the dipole moments and expressions and values for the field parameters are given in Table I.

TABLE I

	Authors	Polder
μ_a	4.19D	4.00D
μ_b	1.42D	3.33D
$A_2^0\overline{r^2} = 12\sqrt{\frac{\pi}{5}}\left[\frac{\mu_a}{a^4} - \frac{\mu_b}{b^4}\right]r^2$	39200 cm^{-1}	24600 cm^{-1}
$A_4^0\overline{r^4} = -20\sqrt{\frac{\pi}{3}}\left[\frac{3\mu_a}{a^6} + \frac{\mu_b}{b^6}\right]r^4$	−28300 „	−33300 „
$A_4^{\pm4}\overline{r^4} = -\frac{5}{3}\sqrt{\frac{35\pi}{2}}\frac{\mu_a}{a^6}\overline{r^4}$	−33000 „	31400 „

In the two different models, the relative magnitudes of A_4^0 and $A_4^{\pm4}$ get reversed. As the crystal field parameters are directly related to the matrix elements of the potential energy, their sign and magnitude essentially determine the ultimate energy levels.

Under the tetragonal field the ^2D state of the Cu^{++} free ion splits into three singlet and one doublet levels. Numerical values of the energies are as follows.

State	Level	Authors	Polder
ϕ_{1a}, ϕ_{1b}	E_{1ab}	7440 cm^{-1}	6606 cm^{-1}
ϕ_0	E_0	2529 ,,	−1363 ,,
ϕ_{2b}	E_{2b}	172 ,,	2224 ,,
ϕ_{2a}	E_{2a}	−17298 ,,	−14143 ,,

In terms of the energy levels the principal g-factors are given by

$$g_i = 2-2\lambda \sum_{n\neq 0} \frac{<0|L_i|n><n|L_i|0>}{E_n - E_0} \quad i = x, y, z$$

Under the present conditions the equations for g reduce to

$$g_z = g_{\parallel} = 2-8\lambda/(E_{2b}-E_{2a})$$
$$g_x = g_y = g_{\perp} = 2-2\lambda/(E_{1ab}-E_{2a})$$

The spin-orbit coupling constant λ is taken as 828 cm^{-1}. Calculated values of $g_{\parallel}$ and $g_{\perp}$ are indicated in Table II along with those obtained by Spence and Kikuchi using Polder's energy values. Experimental values obtained by various investigators are also included in the Table.

TABLE II

	Calculated values		Experimental values			
	Authors	Spence and Kikuchi	Bagguley and Griffiths	Wheatley and Halliday	Arnold and Kip	Authors
$g_{\parallel}$	2.38	2.43	2.40	2.39	2.38	2.41
$g_{\perp}$	2.07	2.08	2.08	2.07	2.05	2.07

In view of the large splittings of the ground state in both the models, the change in the calculated g-values is not very significant. However, a more significant change is obtained in regard to the energies of the various levels. In addition to an overall increase in the splittings due to the crystal field an actual crossing over of the levels ϕ_0 and ϕ_{2b} occurs as one goes from Polder's model to the authors' model owing to a comparatively higher magnitude of the tetragonal parameter.

In conclusion certain approximations which had to be made to make the calculations simple may be clearly stated. The polarisation of the oxygen atoms by the sulphur and other oxygens of the SO_4 group may slightly change its dipole

moment value. The values of $\overline{r^2}$ and $\overline{r^4}$ used in the calculations refer to the values corresponding to the 3*d* electrons only, any overlap between the Cu-3*d* and O-*s*, *p* orbitals being neglected. Finally such an overlap may also introdtice a small change in the value of λ the spin-orbit coupling constant.

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